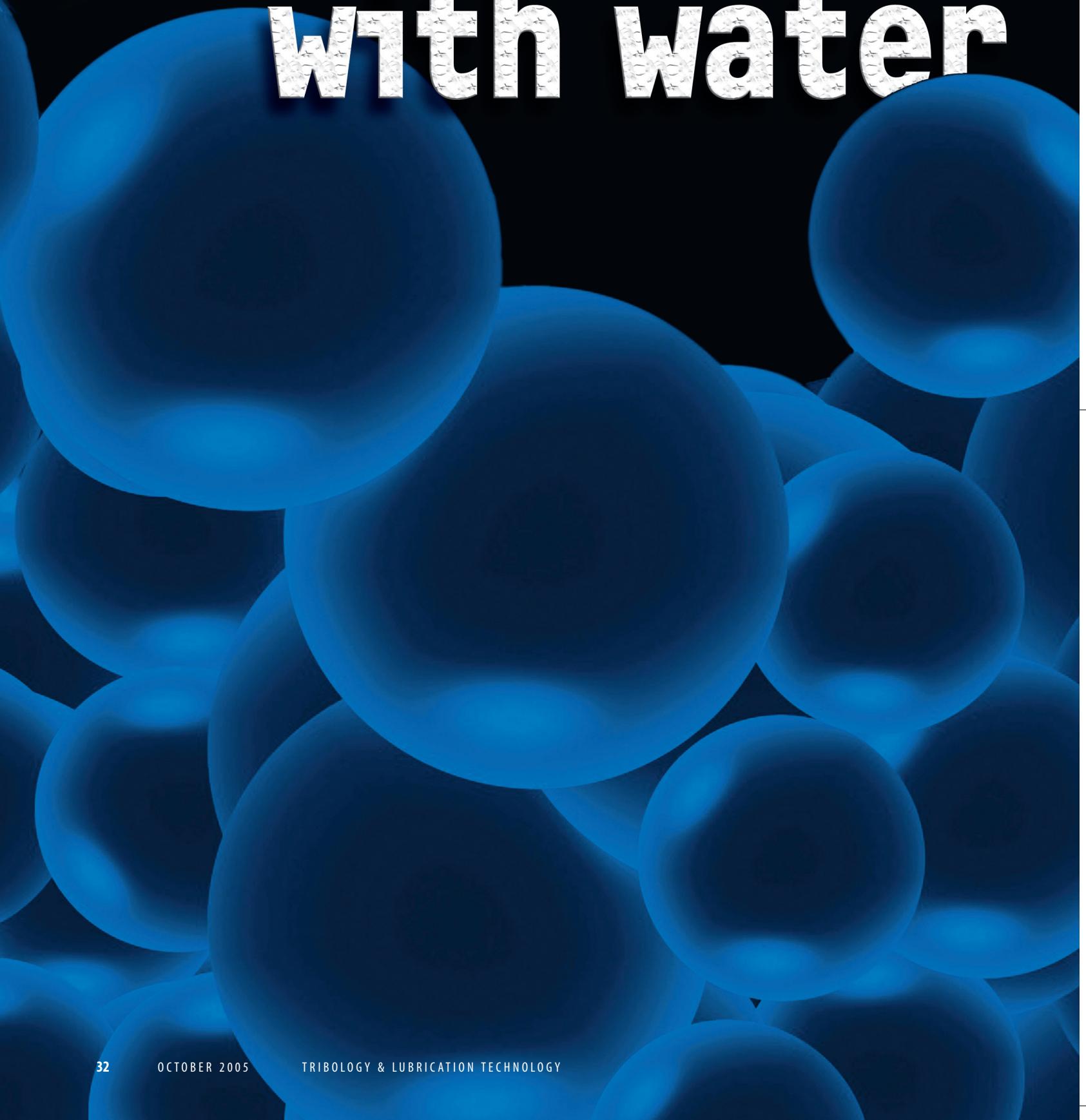


# The trouble with water

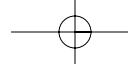


# *'Water, water everywhere, Nor any drop to drink.'*

By Dr. Alan C. Eachus



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## While not as life-threatening as it was to Samuel Taylor Coleridge's Ancient Mariner, the ubiquitous and damaging nature of water can be a true menace to lubricant users.

**Water is one of the two most widespread and destructive contaminants in lubricants, second only to solid particulate contamination.**

Water is one of the two most widespread and destructive contaminants in lubricants, second only to solid particulate contamination. Damage resulting from water contamination is not as immediately noticeable as is that from particulate contamination, but it can be more systemic. Drew Troyer, senior vice president of Global Services Operations for Noria Corp. in Tulsa, Okla., lists five other, less-prominent lubricant contaminants as air, heat, fuel and coolant/antifreeze (in engine lubricants) and radiation.

Water found in lubricants can enter in a number of ways and will be present in the form of dissolved, emulsified (suspended as the internal phase of a water-in-oil emulsion) or free water, with the latter two forms being the most dangerous for lubricated equipment.

### How it gets there

Water can gain access to lubricant systems through improper vents, defective seals or other housing openings or from internal heat exchangers or oil coolers that are leaky or corroded. Loose or even missing storage-tank caps or hatches, or transfer equipment such as hoses and pumps left unprotected when not in use can permit incidental or weather-related water ingress. And in the case of leaked-in steam or splashed-in washdown cleaning solutions, even harsher chemical contaminants can be introduced.

Water is a normal combustion product, and blow-by exhaust gases from combustion processes can sometimes enter lubricant systems. Some lubricants are hygroscopic enough to absorb water vapor directly from the air, and large temperature changes inside a lubricant system result in pressure cycles, permitting humid air to enter an imperfectly sealed oil reservoir in which moisture can then condense. Additionally, virgin lubricants already may be contaminated with some level of water when they are delivered by the manufacturer. Water can exist in new oil as a result of refining, manufacturing or

blending operations, or it can infiltrate in the course of the supplier's transport procedures, handling practices or storage conditions. Bulk-delivered lubricants will be more susceptible to this than will drum-supplied ones. (For information about preventing water ingress from these sources, see "Prevention Methods—How to Keep It Out" on page 37.)

### Adverse effects—the damage it causes

Although the ultimate manifestations of water contamination in lubricants are corrosion, excessive wear and premature failure of lubricated metal surfaces, this destruction is caused in a number of different ways. Water can act directly on metal surfaces and also can impair lubricant effectiveness.

Bubbles of water vapor (or of entrained air) can cause micropitting of bearing surfaces during the course of pressure-caused implosion in which they condense back to liquid phase; this is known as cavitation damage. Moreover, the presence of water in a lubricant can enhance air entrainment therein, setting the stage for more cavitation yet. Water can be adsorbed directly onto hydrophilic metal surfaces, displacing the protective oil layer and even some lubricant additives. This permits direct exposure of the now-unprotected metal surface to corrosive conditions and particulates and results in excessive wear. Free water is especially prone to this sort of behavior.

Another effect of water on metal surfaces is known as hydrogen embrittlement. Water molecules can enter microscopic cracks in metal surfaces through capillary action. Once there, the combination of extreme pressures and free-metal surface contact can cause an almost explosive decomposition of these water molecules into components, one of which is atomic hydrogen. The hydrogen can accumulate in cracks and along metal grains, building up pressure within the metal under conditions of tensile stress and resulting in crack propagation and eventual spalling.

The adverse effects from contaminant water on the lubricant itself can be mani-

fested through physical, chemical and microbiological processes. Since the viscosity of water does not increase with pressure like that of a lubricant, free or emulsified water contained in oil can decrease the effective lubricant viscosity, resulting in insufficient elastohydrodynamic film thickness and inadequate fluid-film strength. This diminished boundary-layer protection can allow rolling or sliding metal surfaces to come into direct contact with each other under high pressure (as in bearing wiping) and cause adhesive wear due to momentary spot-welding of the contacting surfaces.

The overall effect is a lowering of load-carrying ability and a decreased fatigue life of the lubricated surfaces. Moreover, the spot-welded areas are typically sheared off and add to the damaging particulate load. Additionally, a too-thin oil film permits smaller particulate contaminants, which may have passed through an inadequately sized filter, to come directly into contact with moving metal surfaces. The formation of emulsions in a lubricant can lead to creation of sludge and deposits, which can stress pumps and clog orifices, nozzles and jets and blind filters.

Oil oxidation is initiated by the heat, air and pressures encountered in lubricated systems; the presence of water increases this oxidation rate by several times, and the products of oxidation are often acidic and, therefore, naturally corrosive. Further, the presence of particulate contamination together with water contamination can accelerate oxidation rates by at least 50 times.<sup>(1)</sup>

Apparently the metal content of particulate contaminants (iron and copper), together with the surface area of these particulates, provides efficient catalytic promotion of basestock-oxidation reactions. Such enhancement of oxidative conditions also depletes antioxidant additives far more rapidly than would be the case otherwise. Initial oil-oxidation products, such as carboxylic acids and hydroperoxides, will react further, resulting in more sludge and deposits. Unlike mineral oils, some synthetic lubricants are themselves susceptible to hydrolysis. Generally, diesters and phosphate esters are especially prone to hydrolytic decomposition, while polyol esters and polyalkylene glycols are less-readily hydrolyzed; polyalphaolefins (PAOs) demonstrate the best hydrolysis resistance

(Photos courtesy of Pall Corp.)



among synthetic lubricants.

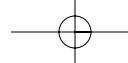
Additives are incorporated into lubricants to serve as viscosity-index improvers, antiwear and extreme-pressure (EP) additives, corrosion inhibitors, antioxidants and foam suppressants. The incorporation of water into oil can change the solubilization characteristics of that oil. Some additives may be de-solubilized and, therefore, precipitated by this change, adding to sludge formation; this physical depletion also renders them unavailable to function effectively in the lubricant. Other additives may be preferentially solubilized by water and "washed out." The incorporation of water-resistance polymers such as high-molecular-weight polyisobutylenes can improve grease washout resistance, notes Wickliffe, Ohio-based, Lubrizol Corp.'s Karen Allen, global business manager for Industrial Business; Debra Light, commercial manager for Hydraulics and Industrial Gear Lubricants; and Matt Sivik, technical manager for Grease Additives.

Even worse, water can react with some additives, not only making them chemically unavailable but also transforming them into such harmful materials as acids or more sludge. As an example, some sulfurized additives can undergo hydrolysis and be converted eventually into such acidic products as hydrogen sulfide or sulfuric acid, leading to etching of bearing surfaces. Similar effects will occur when moisture in a crankcase reacts with the sulfur in fuel-combustion products. Amine-based corrosion inhibition agents can provide significant utility by acting on metal surfaces to help combat acids and prevent the formation of damaging rust particles. Certain hindered-phenolic antioxidants and organophosphite or -phosphate corrosion inhibitors also are sensitive to hydrolysis.

The antiwear additive zinc dialkyldithiophosphate (ZDDP) can be destroyed by

**Water contamination can cause a host of problems, including fluid breakdown, reduced lubricating film thickness, accelerated metal surface fatigue and corrosion. When oil becomes milky in appearance (as in the oil on the right), the saturation limit at the oil temperature has been exceeded, indicating that both dissolved and free water are present.**

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**Because water has such devastating effects, it is vital for the lube user to test for and quantify water contamination and take appropriate steps to remove the water from the oil.**

traces of water at temperatures above about 180 F (82 C). However, Lubrizol personnel point out that varying the dialkyl moiety of ZDDP can assist in stabilizing it against hydrolytic destruction. The impairment of lubrication properties can result in higher operating temperatures, which further exacerbates already-damaging conditions and corrosive wear; an 18 F (10 C) increase in excessive temperature will roughly double oxidation-reaction rates. Moreover, some types of oxidation create more water as a reaction product.

Bacteria and fungi may need as little as 500 ppm of water in the oil environment to grow. The less-than-sterile conditions of lubricant systems, combined with darkness, moisture, moderate (75-120 F, or 24-49 C) temperatures and nutrients supplied by lubricant additives can permit microorganisms to thrive in oil systems. The microbes can degrade additives, induce corrosion and produce biologically derived sludge and deposits that can be as detrimental to system performance as chemically derived ones.

### Determination of water— how much is there?

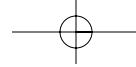
Because water has such devastating effects, it is vital for the lube user to test for and quantify water contamination and take appropriate steps to remove the water from the oil. The level of moisture that can be tolerated in lubricants before water starts to cause serious problems varies widely. For instance, water content of less than 200 ppm (0.02%) will negatively affect roller-element bearing systems, says Troyer; he adds that, "This extreme water sensitivity includes the rolling contact of gear-tooth pitch lines." Conversely, a few thousand ppm of water is needed to seriously degrade engine crankcase oils, with additives playing a major role in permitting contamination tolerance. Many technical reports provide data relating reduced lubricant-moisture content to increased bearing and system life. What is virtually universally agreed is that water levels should be maintained, if possible, below the saturation point of the lubricant, since dissolved water is less damaging than emulsified or free water.

The simplest way to evaluate water content is to visually inspect the oil in question—a hazy or cloudy appearance

can indicate the presence of emulsified water, and free water can be readily noted. Another easy test to perform on-site is the "crackle" test, where a dropperful of lubricant is dropped onto a hotplate preheated to above 100 C. An audible crackling noise, accompanied by bubbles, indicates that the water present is being rapidly driven out of the oil. While trained personnel can quantify water content to well below 1,000 ppm using this procedure, it is probably better used as a qualitative test for the presence of free or emulsified water.

Fourier transform infrared spectrometry (FT-IR) is a well-known procedure for quantifying water content of lubricants and is easy to perform in an appropriate laboratory setting. While some sources suggest that the lower limit of detection for this procedure is about 1,000 ppm, ASTM subcommittee D02.96 is developing a standardized FT-IR test method (currently designated WK6623) that is said to be able to measure lubricant water-levels as low as 50 ppm. The most sensitive test method for water content is the coulometric Karl Fischer titration, which can readily determine moisture levels well below 100 ppm. However, its accuracy can be interfered with by some additives. The current ASTM standard test method for this procedure is designated D6304-04ae1. Other procedures used to determine water levels in oil include measuring the volume of water separated from the oil by centrifuging a sample or distilling off the water in a Dean-Stark apparatus (ASTM D95-05).

Marianne Duncanson, senior tech analyst with ExxonMobil Lubes & Specialties Co. in Friendswood, Texas, states, "By finding trace elements or chemicals in contaminating water, oil analysis labs can often determine its source—whether it is from a steam leak, cooling water, condensation or even rainwater." Sampling for moisture analysis must be done carefully because water is not necessarily distributed throughout a lubricant system homogeneously. Water vapor released by heat at one point can condense in a cooler portion of the system. It's difficult to determine water content of used crankcase lubricants, for example, since the operating temperature of the engine and exhaust will drive off water. Also, extremely low temperatures can convert water into ice crystals, which also may be missed by sampling.



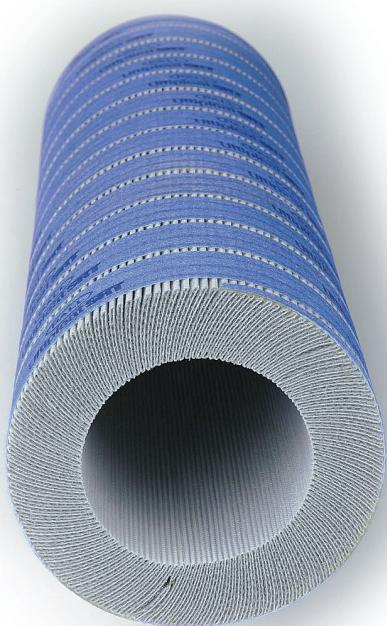
Since it is desirable to maintain moisture levels below the saturation point of the lubricant, water-content data alone are not as useful as knowledge of the lubricant's moisture-saturation value at an appropriate operating temperature and the temperature at various sampling sites, which would permit comparison with the measured system moisture. A lubricant's saturation behavior will be determined by the baseoil (synthetic or mineral), the additive package and the operating temperature. Aged oils will retain more moisture than new ones; API type I hydrocarbon basestocks generally will retain more water in the dissolved state than will type II or type III stocks. Also, polar additives—including detergents and dispersants and some antiwear additives and corrosion inhibitors—raise the saturation point. However, saturation levels at higher operating temperatures can decrease at lower stand-by temperatures, permitting dissolved water to come out of the cooled lubricant as free water.

For typical mineral oils, saturation is often about 200-300 ppm moisture, while

for some synthetic lubricants it can be close to 1,000 ppm. Polar additives play a major role in the ability of a lubricant to maintain water in solution and to hinder demulsibility. For example, the antiwear additive ZDDP and some sulfur-phosphorus EP additives are known to retard demulsibility. For proactive maintenance, manufacturers of on-line moisture-monitoring equipment suggest that action be taken when a lubricant's water level reaches about 70% to 90% of saturation, often 500-1,000 ppm water. Some saturation-meter systems use an oil-inserted probe, while others use saturated relative humidity to calculate water content.

According to Rojean Thomas, engineering manager at Trico Manufacturing Corp. in Pewaukee, Wis., on-line sensors immersed in the oil give an immediate indication if water contamination is entering the system with the oil such as from a water-contaminated lubricant fill or top-off. However, strategically placed airspace

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**According to Pall Corp., which manufactures the Ultipleat SRT filter pictured here, up to 80% of all hydraulic system failures are directly related to dirt and water contamination of fluids, resulting in wear and corrosion of components and leading to breakdown of pumps and valves. Filtration is a frequently chosen solution to the problem of water contamination.**

## Prevention Methods—How to Keep It Out

Preventing water ingress would be preferred to reliance on moisture removal or chemical additization to preserve functionality of a lubricant. However, few lubricant systems can be maintained in a completely water-free state, since they're very seldom totally closed to the outside environment. Thus, minimizing water ingress is important.

Within a piece of lubricated equipment, differential pressures will occur because of thermal expansion and contraction of lubricant fluid or in the course of emptying and refilling the lubricant reservoir. Desiccant breathers can be attached to reservoir and drum vents to prevent moisture-laden air from entering the system under these circumstances. These breathers usually contain silica gel impregnated with cobalt chloride, which acts as a color indicator by changing from blue to pink when the gel is depleted. It is common to also incorporate a particulate filter into such breather contamination-protection systems. In some cases, use of a flexible bladder-type expansion chamber is suitable rather than an outside-environment vent.

The other major equipment-related opportunity for moisture ingress is at the housing seals around rotating shafts, which are meant to retain lubricant and exclude contamination. Lip seals, elastomers which press tightly around a rotating shaft, will exclude moisture when they are new, but the contacting elastomeric surface will wear in the course of service, usually needing replacement after a few months of continuous use despite the presence of a thin film of lubricant at the point of elastomer-shaft contact. It's crucial to ascertain compatibility of not only the base oil but also the additive package, with the elastomeric material, since swelling of the seal will lead more quickly to its failure.

Rotating labyrinth seals consist of two mating, but not truly contacting, parts that create a narrow, convoluted pathway through which moisture and particulates find it difficult to infiltrate. These types of seals should not be used with vertical shafts. Some designs employ an O-ring which lifts off a seat by means of centripetal force during operation and permits expanding air to escape but which reseats to keep out incoming contaminants when the shaft stops turning. Some of the most efficient seals are magnetic seals, usually composed of a stainless steel face adhering magnetically to a polytetrafluoroethylene face; double-faced magnetic seals are even more effective than single-faced ones.

Other steps which can be taken to preclude moisture contamination involve storing drummed or bulk lubricants in a clean, dry and controlled-temperature environment to minimize possible exposure to humidity due to temperature-cycle breathing. Lubricant users should examine their handling and sampling procedures for possible sources of contamination, and caps, hatches and bungs should always be tightened. <<

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**Bubbles of water vapor (or of entrained air) can cause micropitting of bearing surfaces during the course of pressure-caused implosion in which they condense back to liquid phase; this is known as cavitation damage.**

sensors can give immediate warning of vapor-phase moisture such as ingress around a seal or through a vent. Another water-analysis procedure uses the reaction of water with calcium hydride to stoichiometrically produce measurable hydrogen gas. No matter what the lubricant system, lower moisture translates into significantly longer equipment life.

### Removal methods— how to get it out

Several methods, both mechanical and chemical, are available to lower the moisture levels in lubricants to less-destructive levels. The simplest and least effective procedure is settling, wherein free water is allowed to separate from the oil onto the bottom of a containment tank. Heating the oil will increase the rate of settling by lowering the oil's viscosity, but it also can stress the oil by increasing its oxidation rate. Centrifuging the oil physically separates water more rapidly than does gravitational settling but still cannot remove dissolved water. The usual force used here is several thousand G's. Bypass cartridge-type filters also can be employed to remove free and emulsified water from oil, using a hydrophilic fiberglass or derivatized cellulose medium with large surface area. These filters work best with lower-viscosity oils and at constant flow rates. It is important to service filters regularly to ensure optimal functioning.

Two methods permit the removal of dissolved water as well as emulsified and free water. Air stripping involves intimately mixing heated oil with dry air or nitrogen in a high-velocity mixing nozzle. Moisture is removed from the oil through its migration to the dry, flowing

gas, while the dried oil is returned to the lubrication system. Vacuum dehydration combines moderate heating of the oil and a large mass-transfer area with a lowered ambient pressure to efficiently "boil off" dissolved water.

A variation of this technique uses less-severe vacuum and temperature conditions, together with a steadily flowing stream of dry air into which the water transfers. The lubricant can be repeatedly cycled through systems such as these until the desired degree of dryness is reached. Unlike physical methods of water removal, air stripping and vacuum dehydration will not remove non-volatile additives from the lubricant; however, they can remove dissolved gases and volatile hydrocarbons that may be present as contaminants. On the other hand, they also might remove vapor-phase corrosion inhibitors.

Another typical strategy for dealing with oil in water is chemical in nature. Oil-soluble additives called demulsifiers are formulated into many lubricants for which water exposure is likely to be a problem. Demulsifiers are special surfactants that disrupt the oil-water interface surrounding each small, stable water droplet, causing them to coalesce into drops too large to remain suspended in the continuous oil phase (and thus rendering them more amenable to the drying methods just outlined). An example of such chemistry is the class of ethoxylated nonylphenols. ExxonMobil's Duncanson cautions users against adding demulsifiers to a lubricant after formulation, warning, "Demulsifier systems are specific to each lubricant formulation. Moreover, excessive amounts (usually more than 20-50 ppm) can produce an opposite effect." <<

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### For further reading:

- Beercheck, R.C., "How Dirt and Water Slash Bearing Life," *Machine Design Magazine*, July 1978.
- Bloch, H.P. (1980), "Criteria for Water Removal from Mechanical Drive Steam Turbine Lube Oils," *Lubrication Engineering*, **36** (12), pp. 699-707.
- Cantley, R.E. (1977), "The Effect of Water in Lubricating Oil on Bearing Fatigue Life," *ASLE Transactions*, **20** (3), pp. 244-248.
- Duncanson, M., "Detecting and Controlling Water in Oil," *Proceedings of Noria Lubrication Excellence 2005 Conference April 25-29, San Antonio, Texas*.
- Schatzberg, P. and I. Felsen (1968), "Effect of Water and Oxygen During Rolling Contact Lubrication," *Wear*, **12**, pp. 331-342.
- Troyer, D.D. (2001), "Advanced Strategies for the Monitoring and Control of Water Contamination in Oil Hydraulic Fluids," *Hydraulic Failure Analysis: Fluids, Components, and System Effect*, ASTM STP 1339, G.E. Totten, D.K. Will, and D. Feldmann, Eds., American Society for Testing and Materials, West Conshohocken, Pa.

### Reference

- <sup>(1)</sup> Madhavan, P. and Werner, N. C. "Contamination Control for Extending Fluid Service Life," *Practicing Oil Analysis Magazine*, March 2005.